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X-ray determination of thermal expansion of cadmium fluoride and lead fluoride

WAHED HUSSAIN and D B SIRDESHMUKH
Physics Department, Kakatiya University, Warangal 506009, India

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Abstract. The lattice parameters of CdF_2 and β-PbF_2 have been determined over the temperature range 300–670 K. The coefficient of expansion at room temperature is $21{\cdot}3 \times 10^{-6}\,K^{-1}$ and $25{\cdot}4 \times 10^{-6}\,K^{-1}$ for CdF_2 and PbF_2 respectively and it increases linearly with temperature over the range of temperature covered. The Grüneisen parameter decreases with temperature in both the crystals.

Keywords. Thermal expansion; cadmium fluoride; lead fluoride; Grüneisen parameter.

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1. Introduction

Cadmium fluoride and lead fluoride have the fluorite structure in common with the alkaline earth fluorides (CaF_2, SrF_2 and BaF_2). However, in their physical behaviour, they differ in some respects from the alkaline earth fluorides and also with each other. CdF_2 is the only crystal in this group which becomes semiconducting on doping. PbF_2 exists in two phases (α and β) at room temperature; the β phase has the fluorite structure. β-PbF_2 is a prominent representative of the class of materials known as superionic conductors which develop a high electrical conductivity at temperatures close to the melting point. In what follows, the β-phase is implied in all references to PbF_2.

Because of the above mentioned properties, these crystals have attracted considerable attention in recent years and a number of properties have been investigated in detail over a wide range of temperature: ionic conductivity (Samara 1979; Figueroa *et al* 1984), Raman scattering (Elliott *et al* 1978), thermal vibration amplitudes (Koto *et al* 1980); specific heats (Rimai and Sladek 1979), elastic constants (Alterovitz and Gerlich 1970; Manasreh and Pederson 1984). Most of these properties show anomalous temperature variation in the vicinity of the superionic transition temperature.

We are interested in the thermal expansion of these crystals. Some measurements have been made earlier but they cover a limited temperature range and, further, there are substantial differences in the results obtained by different workers. Measurements were made for CdF_2 at low temperatures by Shaharbany *et al* (1976) and at room temperature by Ballard and Browder (1966). Steger and Kostiner (1973) measured the

lattice parameter of CdF_2 at two low temperatures but did not estimate the thermal expansion. The only measurements on thermal expansion of CdF_2 at elevated temperatures are by Krukowska-Fulde and Niemyski (1967). But, as will be shown later, their value at room temperature is too low.

The thermal expansion of PbF_2 has been investigated at low temperatures by White (1980). Using an optical technique, Aurora (Private Communication, 1984) obtained values of the coefficient of thermal expansion which vary linearly with temperature up to very high temperatures. On the other hand, Koto *et al* (1980) from X-ray diffraction measurements found that the temperature variation of lattice parameter clearly indicates a sudden rise as the transition temperature is approached. However, they have not indicated the accuracy of their lattice parameter measurements nor have they calculated the thermal expansion coefficient.

Thus, it is clear that the existing results on thermal expansion of CdF_2 and PbF_2 at elevated temperatures are inconsistent and insufficient. In particular, X-ray measurements of thermal expansion have not been carried out. We have undertaken a systematic measurement of temperature variation of lattice parameters and thermal expansion of these crystals at elevated temperatures. The results for the temperature range 300–670 K are being reported here. The results have been used to calculate the Grüneisen parameter.

2. Experimental

Pure CdF_2 supplied by Koch Light and pure PbF_2 supplied by Reidel de Hahn were used for X-ray diffraction work. Both the substances were in the form of very fine powder. The PbF_2 sample was in the α phase. By heating it for a few hours at 650 K, the β phase was obtained.

For recording the X-ray diffraction photographs, a high-temperature Seeman-Bohlin symmetric focusing camera designed by Sirdeshmukh and Deshpande (1972) was used. With CuK radiation, seven reflection were recorded at high angles for CdF_2 and four for PbF_2. It is known that for a camera with this geometry, $\phi \tan \phi$ is the appropriate error function (ϕ being the complement of the Bragg angle). The lattice parameters were determined accurately by a least-squares extrapolation to $\phi = 0$. X-ray diffraction photographs were obtained at nearly twenty different temperatures in the range 300–670 K.

The temperature variation of lattice parameters as shown in figure 1 is slightly nonlinear. By least squares fitting the following equations were obtained for the lattice parameters (a_T) as a function of temperature (T):

$$CdF_2: \; a_T = 5{\cdot}3550 + 1{\cdot}090 \times 10^{-4}\, T + 1{\cdot}395 \times 10^{-8}\, T^2 \tag{1}$$

$$PbF_2: \; a_T = 5{\cdot}9004 + 1{\cdot}233 \times 10^{-4}\, T + 4{\cdot}629 \times 10^{-8}\, T^2. \tag{2}$$

The values of the lattice parameters calculated from the above equations for a few select temperatures are given in table 1. The room temperature values of the lattice parameter are in fair agreement with those in the ASTM file. The coefficient of

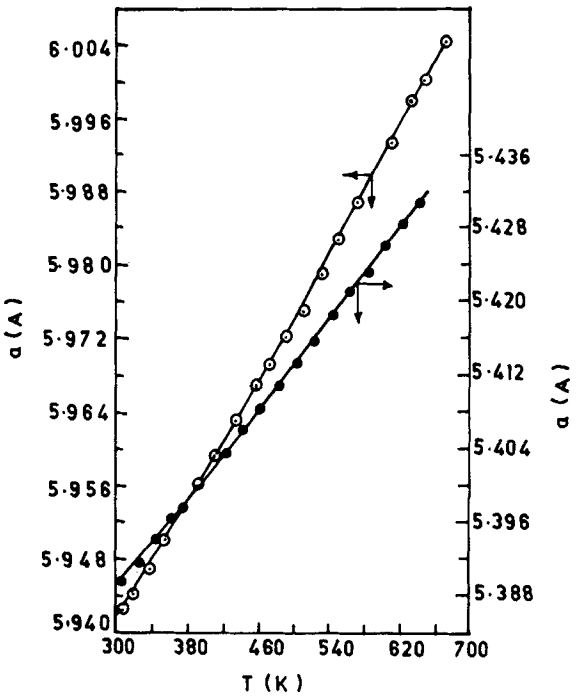

Figure 1. Lattice parameters of CdF_2 (closed circle) and PbF_2 (open circle) at various temperatures.

Table 1. Values of lattice parameters (a), coefficient of thermal expansion (α) and Grüneisen parameter (γ) of CdF_2 and PbF_2 at elevated temperatures.

	a (A)		α (10^{-6} K^{-1})		γ	
T(K)	CdF_2	PbF_2	CdF_2	PbF_2	CdF_2	PbF_2
300	5·3889	5·9416	21·77	25·43	2·30	2·08
350	5·3948	5·9492	22·03	26·20	2·25	2·05
400	5·4008	5·9572	22·29	26·98	2·20	2·01
450	5·4068	5·9653	22·55	27·76	2·16	1·98
500	5·4129	5·9736	22·81	28·54	2·14	1·95
550	5·4191	5·9822	23·07	29·32	2·11	1·92
600	5·4254	5·9911	23·33	30·10	2·09	1·90
650	5·4317	6·0001	23·58	30·88	2·04	1·87

thermal expansion (α) was obtained by differentiating these equations using the definition:

$$\alpha=(1/a_{300})(da/dT). \tag{3}$$

The values of α at some select temperatures are included in table 1. The accuracy in the measurement of various quantities is:

$$a: \pm 0{\cdot}0002\ \text{A}; \quad T: \pm 0{\cdot}5\ \text{K}; \quad \alpha: \pm 0{\cdot}5 \times 10^{-6}\ \text{K}^{-1}.$$

3. Results and discussion

A value of $21{\cdot}8 \times 10^{-6}\ \text{K}^{-1}$ has been obtained for the coefficient of thermal expansion of CdF_2 at room temperature. This compares well with the value of $21{\cdot}3 \times 10^{-6}\ \text{K}^{-1}$ reported by Ballard and Browder (1966). The temperature variation of α of CdF_2 as observed by different workers is shown in figure 2. In the present investigation, a linear temperature variation is observed. The results of Krukowska-Fulde and Niemyski show steep rise in α with increasing temperature followed by a slow linear increase but their value of $13 \times 10^{-6}\ \text{K}^{-1}$ for the thermal expansion at room temperature is too small by any consideration. The present results form a smooth continuation of the low temperature results of Shaharbany *et al* (1976).

A value of $25{\cdot}4 \times 10^{-6}\ \text{K}^{-1}$ has been obtained for the coefficient of expansion of PbF_2 at room temperature. This agrees with the value $25{\cdot}0 \times 10^{-6}\ \text{K}^{-1}$ quoted by Samara (1976) from Morosin's work. The temperature variation of α of PbF_2 is also shown in figure 2. In the present work, a linear temperature dependence is observed.

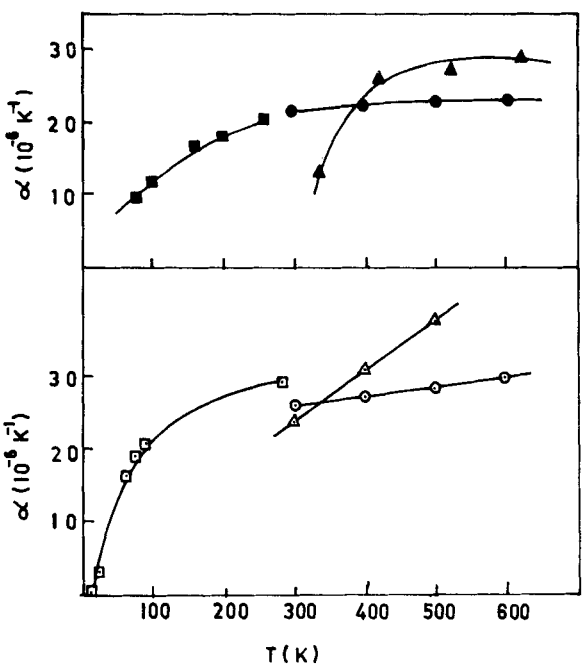

Figure 2. Temperature variation of coefficient of thermal expansion of CdF_2 and PdF_2 (CdF_2: closed circle, present work; closed square, Shaharbany (1976); closed triangle, Krukowska-Fulde and Niemyoki (1967). PbF_2: open circle, present work; open square, White (1980); open triangle, Aurora (1984).

Aurora's (1984) results also indicate a linear temperature variation. But the rate of increase of α with temperature is very much higher in Aurora's data than in the present data. Neither the present results nor Aurora's results form a smooth continuation with White's (1980) low temperature results. However, the present results are closer to White's results than are Aurora's results.

The Grüneisen parameter (γ) has been calculated from the relation:

$$\gamma = 3\alpha V/\psi_T C_v \tag{4}$$

where V is the molar volume, ψ_T the isothermal compressibility and C_v the molar specific heat. α and V (calculated from the lattice constant) are from the present measurements. ψ_T is calculated from the data on temperature variation of elastic constants obtained by Alterovitz and Gerlich (1970) for CdF_2 and Manasreh and Pederson (1984) for PbF_2. Values of C_v are calculated from the Debye function using the Debye temperatures 328 K (Hayes 1974) and 237 K (Dandeker *et al* 1979) for CdF_2 and PbF_2 respectively. The value of γ for some temperatures are given in table 1.

The Grüneisen parameter shows dramatic changes with temperature at very low temperatures. At elevated temperatures, the variation is generally very slight and smooth. Rapp and Merchant (1973) found that in the alkali halides γ increases very slowly with temperature. Slack and Huseby (1982) found that at elevated temperatures, γ is independent of temperature in the case of a number of phenacyte-type compounds. In CaF_2, Ho and Ruoff (1967) found that γ decreases with temperature. Similarly, in the case of ThO_2, Momin and Karkhanavala (1978) observed a decrease in γ with increasing temperature.

The temperature variation of Grüneisen parameter of CdF_2 and PbF_2 at elevated is shown in figure 3. The Grüneisen parameter shows a slight decrease with increasing temperature. In the range 300–650 K, the decrease in γ is about 10% in both the compounds. Qualitatively, the trend in temperature variation of γ in these crystals is similar to that observed in related crystals CaF_2 and ThO_2, as discussed in the preceding para. Since in superionic conductors anomalous temperature variation is observed in many physical properties near the transition temperature, both α and γ may also exhibit anomalous variation. Measurements of the lattice parameters and thermal expansion of CdF_2 and PbF_2 at temperatures approaching the transition temperature are on hand and the results will be published separately.

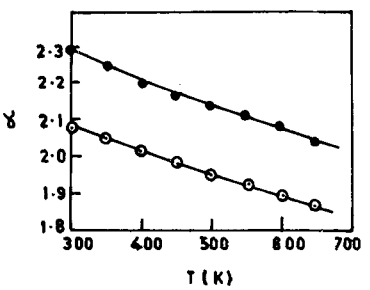

Figure 3. Grüneisen parameters of CdF_2 (closed circle) and PbF_2 (open circle) as a function of temperature.

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References

Alterovitz S and Gerlich D 1970 *Phys. Rev.* **B1** 4136
Ballard S S and Browder J S 1966 *Appl. Opt.* **5** 1873
Dandekar D P, Tsou J J and Ho J C 1979 *Phys. Rev.* **B20** 3253
Elliott R J, Hayes W, Klappmann W G, Rushworth A J and Ryan J F 1978 *Proc. R. Soc. London* **A360** 317
Figueroa D R, Fontanella J J, Wintersgill M C and Andeen C G 1984 *Phys. Rev.* **B29** 5909
Hayes W 1974 *Crystals with fluorite structure* (Oxford: Clarendon Press)
Ho P S and Ruoff A L 1967 *Phys. Rev.* **161** 864
Koto K, Schulz H and Huggins R A 1980 *Solid State Ionics* **1** 355
Krukowska-Fulde B and Niemyski T 1967 *J. Cryst. Growth* **1** 183
Manasreh M O and Pederson D O 1984 *Phys. Rev.* **B30** 3482
Momin A C and Karkhanavala M D 1978 *High Temp. Sci.* **10** 45
Rapp J E and Merchant H D 1973 *J. Appl. Phys.* **44** 1973
Rimai D S and Sladek R J 1979 *Solid State Commun.* **31** 473
Samara G A 1976 *Phys. Rev.* **B13** 4529
Samara G A 1979 *J. Phys. Chem. Solids* **40** 509
Slack G A and Huseby I C 1982 *J. Appl. Phys.* **53** 6817
Shaharbany D 1976 *Thermal expansion of cadmium fluoride* M.Sc. thesis, Tel Aviv University
Shaharbany D, Wolf M and Gerlich D 1976 *J. Phys. Chem. Solids* **37** 577
Sirdeshmukh D B and Deshpande V T 1972 *Proc. Indian Nat. Sci. Acad.* **38** 167
Steger J and Kostiner E 1973 *J. Chem. Phys.* **58** 3389
White G K 1980 *J. Phys.* **C13** 4905